Influence of organic additives on the surface characteristics of zinc electrodeposition on mild steel in acid-chloride solution: ph, bath-composition and time-variation effects

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EXPERIMENTS have been performed to examine the electrodeposition of zinc on mild steel in acid-chloride solutions, using as additives different concentrations of thiourea, either alone or in combination with dextrin. The experiments were performed under variable pH and plating-time conditions, and the ultrasonically-cleaned steel surface (film) was analysed for surface composition/impurities by ESCA (electron spectroscopy for chemical analysis) instrumentation. Zinc electrodeposition on mild steel was performed using a DC-supply at defined operating parameters, the surface of the plated steel being examined using scanning-electron microscopy (SEM). Different surface characteristics were obtained depending upon the pH, plating time and bath composition, but the quality of the electrodeposition of zinc was good.

Introduction

In a recent report[1], the effects of some organic additives on the electrodeposition of zinc on mild steel in acid-chloride solutions were demonstrated using scanning-electron microscopy (SEM). The present work, which is an extension of that mentioned above, looks further into the influence of organic additives on the surface characteristics of zinc electrodeposition on mild steel in acid-chloride solutions with varying pH, bath composition and plating times.

The growth in popularity of acid zinc-based baths in the past few years has resulted from the need to avoid the toxicity of cyanide-based baths and their costly effluent following stringent regulations against water pollution. Though commercially-available proprietary additives[2-5] have now been used for some years, the need to develop other non-commercial proprietary additives for the acid-chloride bath has generated the present interest in further research. The organic additives used in this work have been previously used in different forms as constituents of additives in acid-sulphate baths[6-10].

Results from the previous investigation[1] would indicate that the quality of zinc electrodeposition on mild steel in acid-chloride solution, when thiourea, dextrin and glycin are used as the additives, is good. It is expected that improved results will be obtained in this work, though problems associated with the operating parameters are not unexpected. In this paper, the terms 'plating' and 'electrodeposition' are interchangeable. This work makes a further contribution to the existing knowledge of additives in zinc electrodeposition and hence to the corrosion-prevention field in general.

Experimental procedure

Preparation of test specimens and solutions

A (Swedish-made) mild steel SIS 1411-47, with a nominal composition of 0.038% C, 0.19% Mn and the rest Fe, was used for the experimental test specimens. Otherwise the preparatory procedure was as previously described[1].

The 1-mm thick and 10-mm wide flat steel plate was cut into several test specimens, each 100mm long. A 10-mm length was marked off at one end of each specimen for the electrodeposition of zinc, this being the portion that was inserted into the plating solution.

Henkel VR 6362-1, a commercial alkaline degreasing chemical, was used to degrease the test specimens ultrasonically for about 5min. The specimens were removed from the cleansing solution, rinsed in distilled water, immersed in

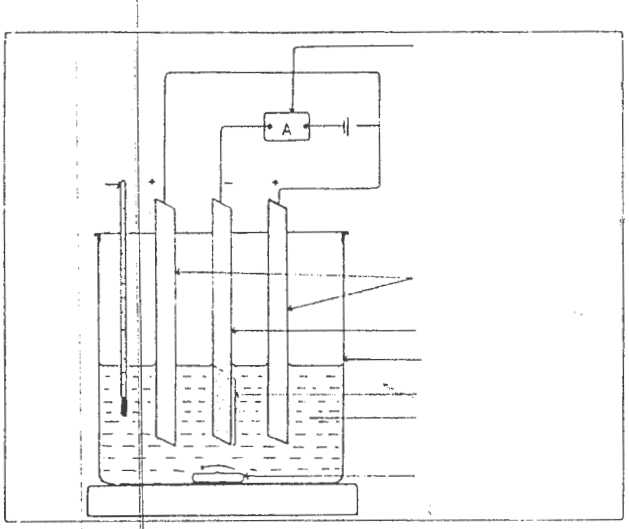

Fig.1. The experimental set-up.

methanol and air-dried. The specimens were then etched in turns for 30sec each in 3M HCl at 50°C, again rinsed in distilled water, immersed in methanol and air-dried, before being stored in a desiccator for later use in electrodeposition.

The acid-chloride solution for the electrodeposition process consisted of ZnCl - 71g/l; KCl - 207g/l, and H_3BO_3 - 34g/l. Three different solutions were made together with addition agents as follows: acid-chloride solution plus thiourea 0.10g/l; acid-chloride solution plus thiourea 0.10g/l and dextrin 3.0g/l; acid-chloride solution plus thiourea 0.10g/l and dextrin 0.3g/l.

Duplicates of each of these solutions were prepared in turn and adjusted, from the existing pH4 of the original solutions to pH5 by using zinc hydroxycarbonate solution.

ESCA analysis of the steel surface

The surface of the steel test specimen was analysed using ESCA instrumentation to determine the composition of the steel's surface film prior to electrodeposition of zinc in the acid-chloride solution. The cut portion (5 x 8mm) of the alkaline-degreased and HCl-etched test specimen was put in an ESCA *HP 5958A* and the steel's surface was analysed using X-ray photoelectron spectroscopy (XPS). Further sputtering of the film to a depth of 3A was made by Ar^+ ion etching to allow an in depth study of the composition of the steel's surface film.

Electrodeposition of zinc on steel

The same procedure was followed as has been previously described[1]. The steel specimen and the zinc electrodes were immersed in the plating solution as shown in Fig.1. A thermometer was used to measure the bath temperature.

The steel specimen was connected to the negative side of a DC-supply while the zinc was connected

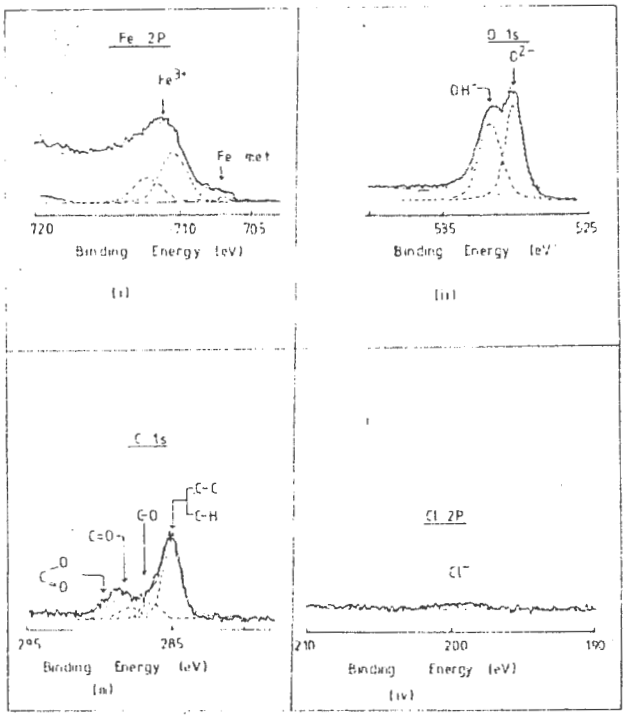

Fig.2. ESCA spectra recorded from the surface of the degreased and etched mild-steel test specimen.

to the positive side. The two zinc electrodes were also connected to each other with a wire. The pH of each plating solution was measured with a pH meter and solutions with pH of 4 and 5 were used in turns. Two different plating-times of 12.5min and 30min were also used in turns. All the plating was carried out within a temperature range of 27-30°C using a current of 30mAcm^{-2} while the solution was stirred gently.

After each plating the specimen was taken out of the bath, rinsed in distilled water, immersed in methanol and quickly air-dried for onward examination in the SEM.

SEM examination

A small portion cut off each plated-steel specimen was mounted on a stub and each was examined in the SEM; micrographs were made of the representative areas of the surface at the x100 and x1000 magnifications.

Results and discussion

ESCA spectra

The ESCA spectra, Fig.2, recorded from the surface of the degreased steel specimen before electrodeposition, are the same as previously reported[1]. The signals obtained from the elements detected on the surface film, that is, iron, oxygen, chloride and carbon, were differentiated - oxygen and iron each into two separate peaks.

Oxide (O^{2-}) and hydroxide (OH^-) ions on the surface of the steel are represented by two peaks of the oxygen signal. The two peaks of the iron signal

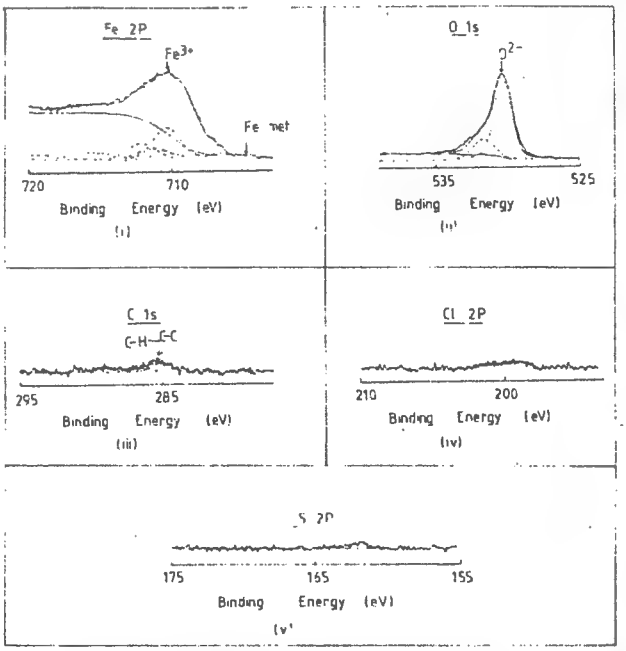

Fig.3. ESCA spectra recorded from the surface of the degreased and etched mild-steel test specimen after supttering with Ar^+.

represent Fe^{3+} and Fe^{2+}, with the Fe^{3+} predominating. The chloride (Cl^-) signal is believed to come mainly from the HCl which was used to etch the metal specimen, and the signal shows no change. The carbon signal is believed to have resulted from the methanol that was used to rinse the specimen after etching and before air drying.

Sputtering of the surface film by Ar^+ to an etching depth of 3A, Fig.3, indicates that OH^- is only present on the surface. There was a chemical shift in which the OH^- signal almost disappeared. The peaks representing carbon and chloride were obtained at very low intensity levels; the source of the low-intensity sulphur signal obtained after ion etching is not clear. It might have originated from the commercial alkaline degreasing chemical used for cleaning the steel specimens.

The plating medium is very acidic and this could destroy the surface film of the metal. It is therefore not expected that the composition of the surface film would significantly affect the characteristics of zinc electrodeposition on the steel.

Effects of plating time and pH

The effects of plating time and pH on the surface characteristics of the electrodeposited zinc on mild steel in the plating solution can be discussed, based on the different additives used. The SEM micrograph of the surface of the mild steel test sample before electrodeposition is shown in Fig.4.

(i) Addition of thiourea (0.10g/l)

The effect of plating time when thiourea alone (0.10g/l) was added to the acid-chloride solution at

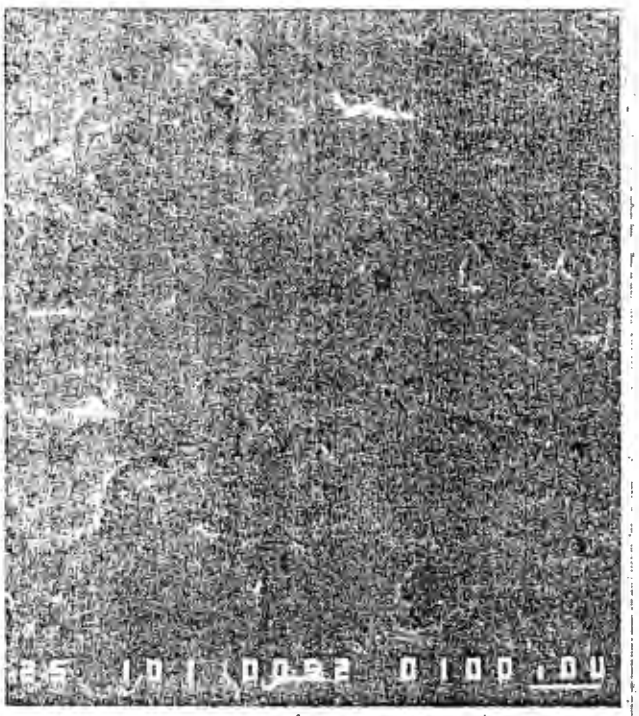

Fig.4. SEM micrograph of the etched surface before zinc electrodeposition.

pH4 is presented in Figs 5 and 6; the effect at pH5 is presented in Figs 7 and 8. There is not much difference between the characteristics of the electrodeposited zinc on the mild steel in Fig.5, which represents a plating time of 12.5min, and in Fig.6, which represents 30min of plating. However, the crystal grains of the latter seem to be larger than those of the former. This phenomenon will be due to the increasing growth of the crystals with time. It is also observed that at pH4, the addition of thiourea (0.10g/l) did not give good plating. Microscopically large pores are present on the zinc-electrodeposited surface of the mild steel; this is difficult to explain at present.

Nevertheless, it is generally known that zinc electrodeposition from acid-chloride solution is sensitive to the prevailing pH level at different bath concentrations of the additives.

A totally different observation from the above is indicated in Fig.7, which represents a plating time of 12.5min, and in Fig.8, which represents a plating time of 30min. Good zinc electrodeposition with finer crystal-grain structures are obtained, though there are some pores, as can be seen in Figs 7(i) and 8(i). However, there is yet another striking difference between the grain structures of Figs 7(ii) and 8(ii): the grain crystals in the latter are far coarser than those of the former. This is due mostly to the effect of plating time - a further confirmation that the longer the plating time, the bigger or coarser the grain crystals resulting from crystal growth.

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The difference in grain structure, porosity and surface morphology is marked between in Figs 5 and 6 on the one hand (representing plating at pH4) and Figs 7 and 8 on the other (representing plating at pH5). The grain structures in the latter are very much smaller and finer, compact, morphologically smoother, and much less porous when compared to the former. This is an indication that for this bath composition, and with respect to the different plating times, plating at pH5 is more appropriate and hence more effective for zinc electrodeposition on mild steel.

(ii) Addition of thiourea (0.10g/l) and dextrin (3.0g/l)

The SEM micrographs made from the zinc-electrodeposited surface of mild steel in an acid-chloride solution with the addition of thiourea (0.10g/l) and dextrin (3.0g/l) at pH4 are shown in Figs 9 and 10 after a plating time of 12.5min and 30min respectively, while Figs 11 and 12 represent the micrographs made at pH5 - also with plating times of 12.5min and 30min respectively. At the low magnification of x100, Figs 9(i) and 10(i), the difference in structure is not apparent with respect to plating time. The plating appears good in both, as there is no trace of microscopic pores. However, at the greater magnification of x1000, Figs 9(ii) and 10(ii), though the structures are similar, the grain sizes are different. At the plating time of 12.5min (Fig.9ii), the grain crystals are finer or smaller in size than in Fig.10(ii) for which the plating time was 30min, showing that the grain size increases with increasing plating-time. If larger grain size leads to plating microcracks, the shorter plating time of 12.5min may be preferable in order to minimize grain size.

Similarly, in Figs 11 and 12 which represent plating at pH5 after 12.5min and 30min, and at high (x1000) and low (x100) magnifications respectively: there is no observed occurrence of pores - an indication of good plating. It is extremely difficult to explain the difference in structure and grain sizes in both figures at the low-magnification level. However, at the higher magnification (x1000), a difference in grain crystal structures is indicated. This is not just in terms of grain size alone, as previously observed, but also in grain orientation and form. The only different factor between the two is the time factor. Fig.11 has more of an elongated and directionally-orientated grain structure, while Fig.12, which is not so well defined, has a coarser structure mixed with irregularly-shaped, smaller, grain crystals. Further growth in grain crystals due to time would have caused the observed difference.

Figs 9 and 11 (resulting from a plating time of 12.5min) and Figs 10 and 12 (resulting from a plating time of 30min) could be compared to show the effect of pH on the surface characteristics of the electrodeposited zinc. At a magnification of x100, the difference in structure for Figs 9 and 11 is very difficult to describe, as no particular feature is clearly indicated. However, at a magnification of x1000, the structural difference is apparent. At pH4, the grain crystals are well-defined, like piles of plate-like slabs in different orientations; while at pH5, the grains are elongated and not well-defined, but appear smoother. It is difficult to say at present what effect these two different structures have on the properties of the plated surface. With respect to Figs 10 and 12, though the plating-time was the same, the grain structures are still very different due to the effect of pH. It is clear that at pH4 (Fig.10) the grain crystals are better-defined in terms of shape, form, orientation, compactness and size than at pH5 (Fig.11). If these attributes are to be strictly followed, it can then be inferred that plating at pH4 could give better surface-plating characteristics.

(iii) Addition of thiourea (0.10g/l) and dextrin (0.3g/l)

Figs 13 and 14 show the SEM micrographs as a result of the addition of thiourea (0.1g/l) and dextrin (0.3g/l) on the electrodeposition of zinc on mild steel in acid-chloride solution at pH4 and plating times of 12.5min and 30min respectively. Figs 15 and 16 indicate the SEM micrographs made at plating times of 12.5min and 30min respectively. These similarly show the effect of the above-mentioned additives on the zinc-electroplated surface of the mild steel at pH5.

In Figs 13 and 14, at both low (x100) and high (x1000) magnifications, there were no visible surface pores - an indication of uniform and good electrodeposition of zinc on the mild-steel specimens.[4]

In Fig.13, the grain structure is finer than the grain structure of Fig.14. Again, the coarser nature of the crystal grains in the latter is due to the prolonged plating time that encouraged growth in size of the crystals. In electrodeposition, the finer surface grain is preferred as it offers better surface properties in terms of microcracks and electrodeposition stability. Similarly, the grain structure in Fig.15 (plating time of 12.5min) is finer and better-defined than that in Fig.16 (30min plating time) under the same condition of pH5. The two grain structures are very different morphologically.

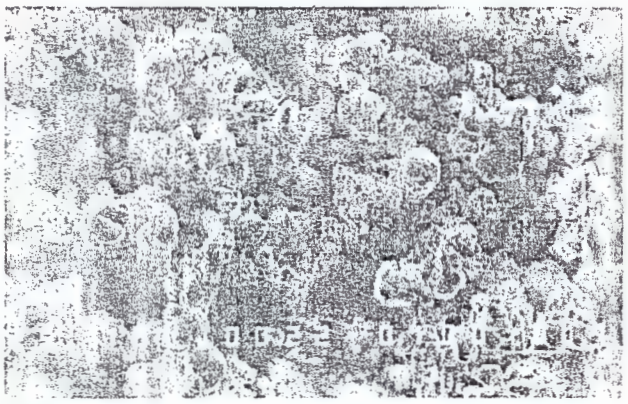
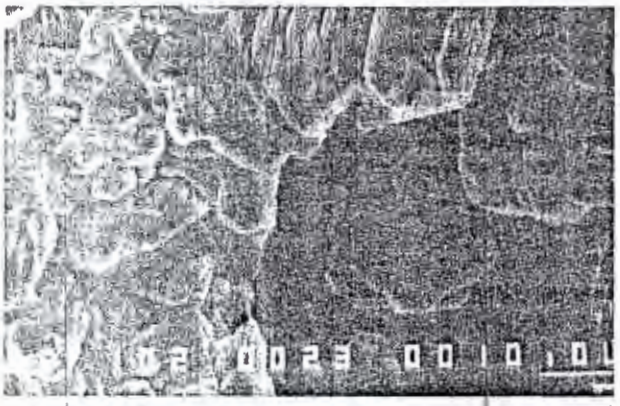


Fig.5. SEM micrographs showing the effect of thiourea addition on the electrodeposition of mild steel in acid chloride solution at ph = 4 and a plating time of 12.5mins. (Note: above = x 100; below = x 1000).

Fig.6. SEM micrographs showing the effect of thiourea addition on the electrodeposition of mild steel in acid chloride solution at ph = 4 and a plating time of 30mins. (Note: above = x 100; below = x 1000).



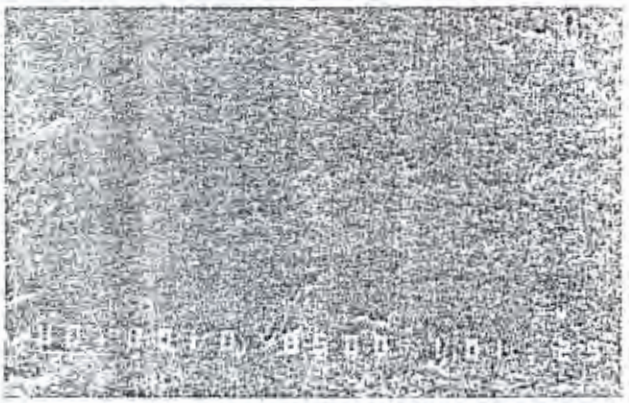
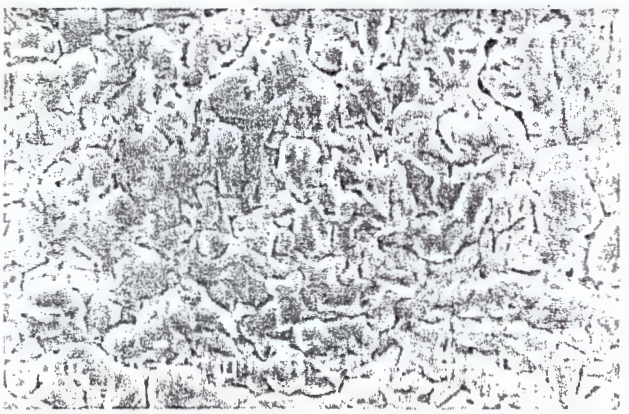


Fig.7. SEM micrographs showing the effect of thiourea addition on the electrodeposition of mild steel in acid chloride solution at ph = 5 and a plating time of 12.5mins. (Note: above = x 100; below = x 1000).



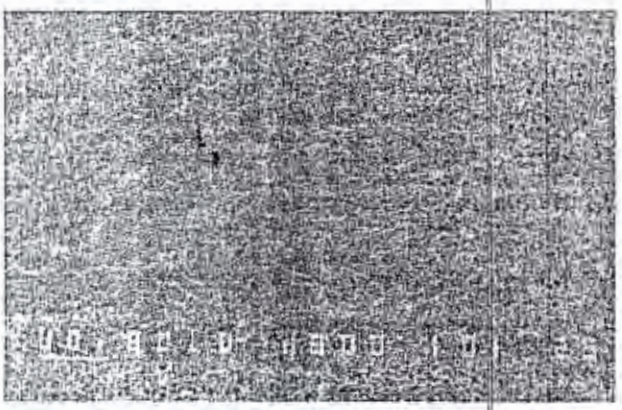


Fig.8. SEM micrographs showing the effect of thiourea addition on the electrodeposition of mild steel in acid chloride solution at ph = 5 and a plating time of 30mins. (Note: above = x 100; below = x 1000).

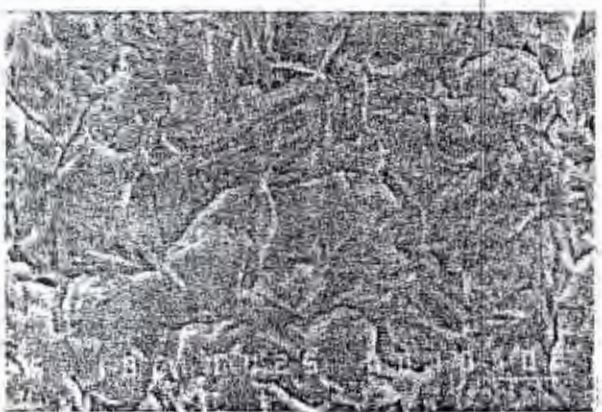
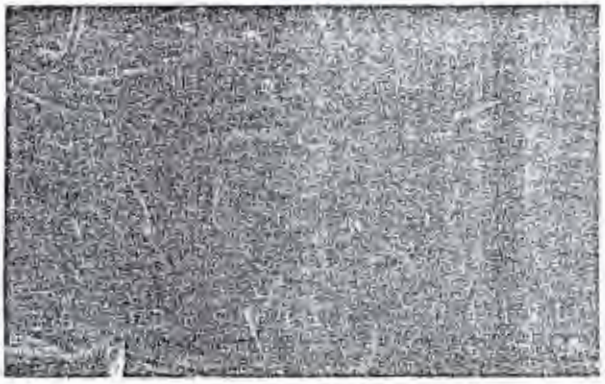


Fig.9. SEM micrographs showing the effect of thiourea (0.1g/l) and dextrin (3.0g/l) addition on the electrodeposition of mild steel in acid chloride solution at ph = 4 and a plating time of 12.5mins. (Note: above = x 100; below = x 1000).

Fig.10. SEM micrographs showing the effect of thiourea (0.1g/l) and dextrin (3.0g/l) addition on the electrodeposition of mild steel in acid chloride solution at ph = 4 and a plating time of 30mins. (Note: above = x 100; below = x 1000).



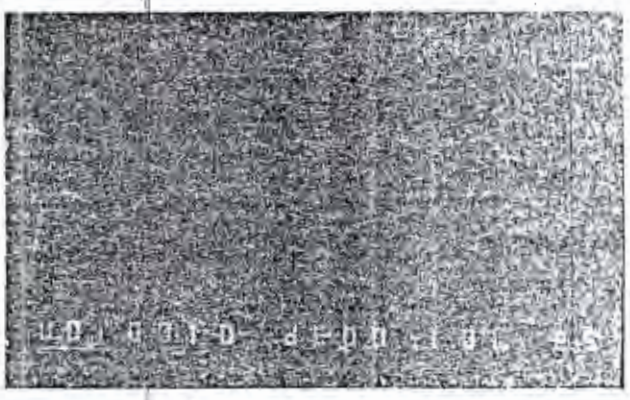


Fig.11. SEM micrographs showing the effect of thiourea (0.1g/l) and dextrin (3.0g/l) addition on the electrodeposition of mild steel in acid chloride solution at ph = 5 and a plating time of 12.5mins. (Note: above = x 100; below = x 1000).

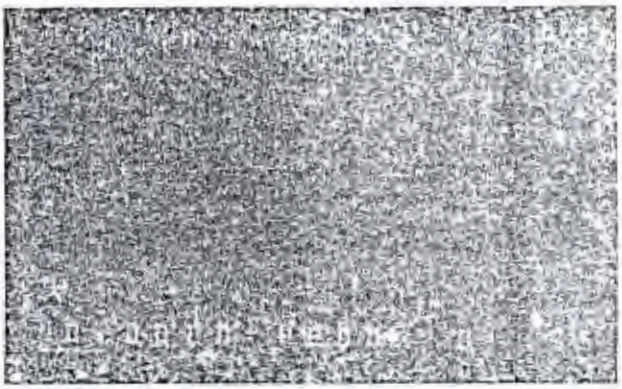
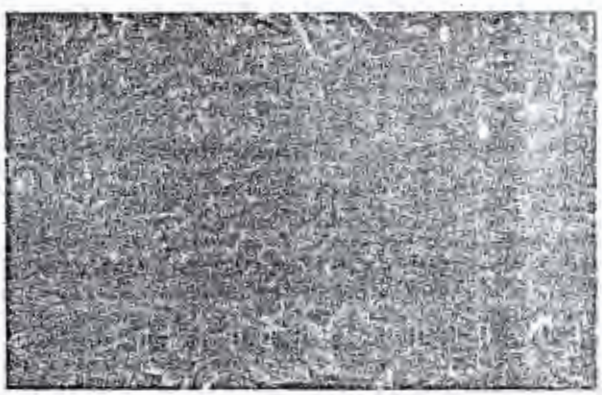


Fig.12. SEM micrographs showing the effect of thiourea (0.1g/l) and dextrin (3.0g/l) addition on the electrodeposition of mild steel in acid chloride solution at ph = 5 and a plating time of 30mins. (Note: above = x 100; below = x 1000).



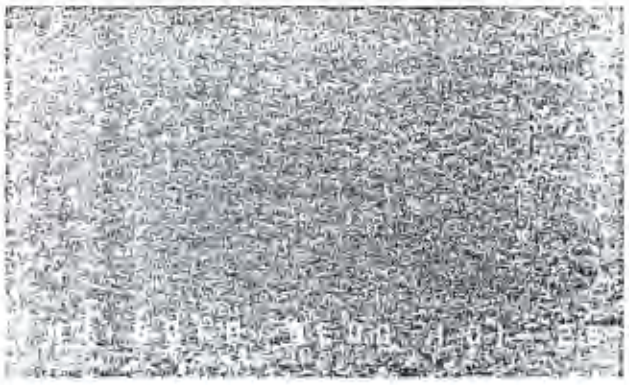


Fig.13. SEM micrographs showing the effect of thiourea (0/1g/l) and dextrin (0.3g/l) addition on the electrodeposition of mild steel in acid chloride solution at ph = 4 and a plating time of 12.5mins. (Note: above = x 100 below = x 1000).

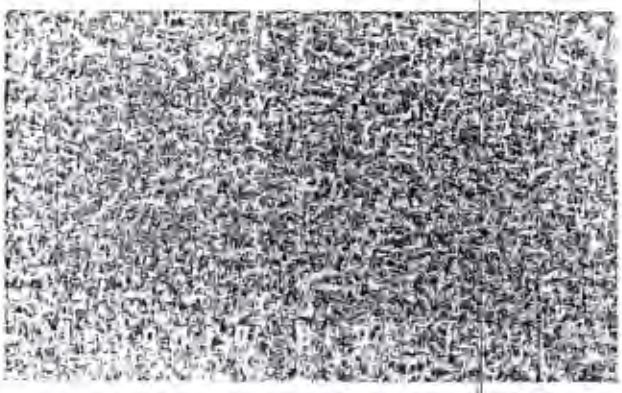
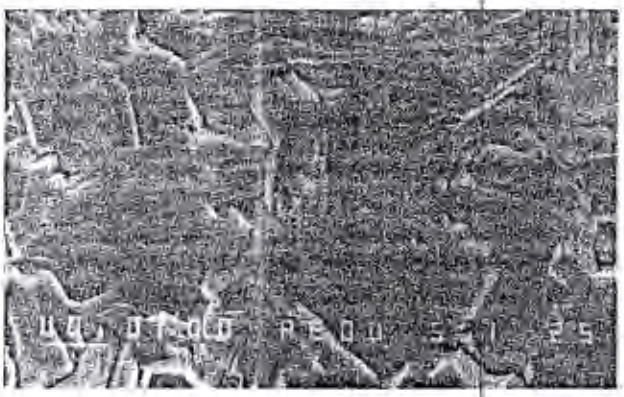


Fig.14. SEM micrographs showing the effect of thiourea (0/1g/l) and dextrin (0.3g/l) addition on the electrodeposition of mild steel in acid chloride solution at ph = 4 and a plating time of 30mins. (Note: above = x 100; below = x 1000).



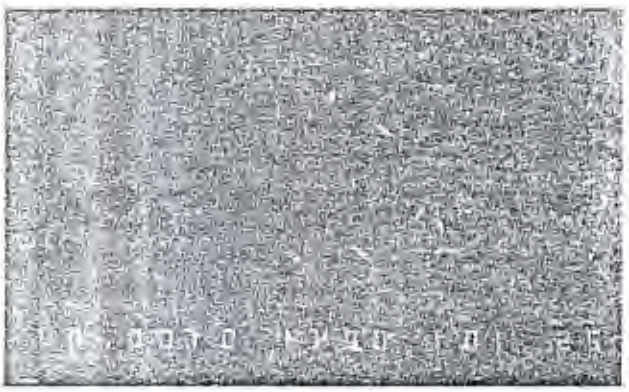


Fig.15. SEM micrographs showing the effect of thiourea (0/1g/l) and dextrin (0.3g/l) addition on the electrodeposition of mild steel in acid chloride solution at ph = 5 and a plating time of 12.5mins. (Note: above = x 100; below = x 1000).

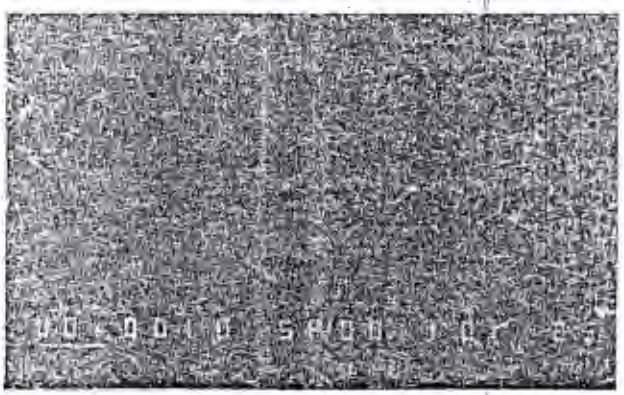


Fig.16. SEM micrographs showing the effect of thiourea (0/1g/l) and dextrin (0.3g/l) addition on the electrodeposition of mild steel in acid chloride solution at ph = 5 and a plating time of 30mins. (Note: above = x 100; below = x 1000).

The effect of pH on the surface characteristics of the electrodeposited zinc can be determined from an analysis of Figs 13 and 15, each representing a plating time of 12.5min, and pH4 and pH5 respectively. Figs 14 and 16, each representing a plating time of 30min and pH4 and pH5 also show the pH effect by comparison.

At low magnification (x100), the difference in structure of Figs 13 (at pH4) and 15 (at pH5) is not clear. However, at a higher magnification (x1000), the grain structure of Fig.15 can be seen to be finer and more evenly distributed than that in Fig.13, though the latter's crystal grain is also well distributed. Both grain structures will give good plating-surface properties.

Figs 14 and 16 (each at pH5 and 30min plating time), present structures of coarse-grain crystals. Though looking alike, the grain crystals of Fig.14 appear more defined in piled plate-like form than in Fig.16, which has similar appearance but with elongated-grain structure.

It is apparent from the above results and discussion that plating time and pH have profound effects on the surface characteristics of zinc electrodeposition on mild steel in acid-chloride solution with thiourea and dextrin as additives.

Effect of bath composition

The effect of bath composition on the surface characteristics of zinc electrodeposition on mild steel in acid-chloride solution can be discussed based on the different additives and their concentrations as reported above.

The addition of thiourea (0.10g/l) to the acid-chloride solution at pH4 at the plating times of 12.5min and 30min respectively (Figs 5 and 6) did not give good plating. This was either because the pH4 solution is not suitable for the electrodeposition of zinc, or because the plating-operating parameters could not be optimized or improved despite several repetitions of the experiment. At pH5, at the plating times of both 12.5min and 30min, the zinc electrodeposition obtained was fairly good for that bath composition.

Further addition of thiourea (0.10g/l) and dextrin (3g/l) gave much improved zinc electrodeposition on mild steel, as shown in Figs 9 and 12. These results show that dextrin, at that concentration, has a complementary effect in combination with thiourea, giving very good plating.

When the concentration of dextrin was reduced from 3g/l to 0.3g/l in combination with thiourea (0.10g/l), and was added to the acid-chloride solution, another very good zinc electrodeposition was obtained, as shown in Figs 13 to 16. This was not apparently different in grain structures from that obtained by the addition of thiourea (0.10g/l) and dextrin (3g/l), at the same plating time and pH. Since the characteristic levelling nature of thiourea is not very apparent in any of the micrographs, it can then be justifiably asserted that dextrin has a more predominant effect on the surface characteristics of the electrodeposition of zinc throughout this work, at different concentrations and in combination with thiourea. The predominant effect of dextrin is definitely due to the very low concentration of thiourea used.

Further work on the effect of different combinations of additives at relatively higher concentrations and variable pH but constant time, will be the subject of a future report.

Conclusions

1. Characterization of the zinc-plated surface of the mild steel specimens revealed different surface features depending upon the plating conditions used.
2. The pH, plating-time, and bath-composition variations have different effects on the grain crystal structure of electrodeposited zinc on mild steel. For example, the longer the plating time, the coarser the grain crystals.
3. At the different concentrations used, the thiourea and dextrin displayed complementary plating effect and produced good plating results at the different pH and plating times employed. The plating is compact, non-porous, and the grains are fine at a plating time of 12.5min.
4. Though not as bright as the cyanide bath, the surface structures obtained indicate that the plating can serve several useful protective purposes.

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